PB84-200948

Wastes from Manufacture of Dyes and Pigments
Volume 8. Phthalocyanine Dyes and Pigments

SRI International, Menlo Park, CA

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-200948

EPA-600/2-84-111h
June 1984

WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 8. PHTHALOCYANINE DYES AND PIGMENTS

By

David C. Bomberger

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Contract 68-03-2944
Task 1, Subtask 4

Project Officer
Mark J. Stutsman
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-84-111h	2.	3. RECIPIENT'S ACCESSION NO. PB84 200948
4. TITLE AND SUBTITLE WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOL. 8: PHTHALOCYANINE DYES AND PIGMENTS		5. REPORT DATE June 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) David C. Bomberger		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Ave. Menlo Park, CA 94025		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-03-2944
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research & Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

A preliminary study of the manufacture of phthalocyanine dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and six companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 36
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of the segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

A preliminary study of the manufacture of phthalocyanine dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and six companies that produce representative dyes and pigements are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report was submitted in fulfillment of Contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period December 9, 1981 to June 15, 1982, and work was completed as of October 30, 1983.

CONTENTS

FOREWORD iii

ABSTRACT iv

TABLES vi

1. INTRODUCTON 1

2. SUMMARY AND CONCLUSIONS 4

3. PROCESS CHEMISTRY 5

Preparation of Copper Phthalocyanine by the Phthalic Anhydride/Urea Process 6
Preparation of Halogenated Phthalocyanines 7
Pigment Processing 8
Preparation of Sulfonated Phthalocyanines 9
Reactive Dyes 10

4. ORGANIC AND INORGANIC INTERMEDIATES, REAGENTS, AND CATALYSTS USED IN PHTHALOCYANINE DYE AND PIGMENT PRODUCTION 13

5. SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING 16

Overview of Dye and Pigment Production Processes 16
Materials in the Waste Streams from Phthalocyanine Dye and Pigment Production 18

REFERENCES 27

TABLES

Number

1. Phthalocyanine Dyes and Pigments Included in This Study..... 2

2. Organic and Inorganic Chemicals Required for the Manufacture of Phthalocyanine Dyes and Pigments..... 14

3. Organic Materials that May Appear in the Waste Streams from the Production of Phthalocyanine Dyes and Pigments of Known Manufacturing Process..... 20

4. Directory of Dye and Organic Pigment Manufacturers, 1979..... 22

5. 1979 Producers of Phthalocyanine Dyes and Pigments..... 24

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this study is to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain signficant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes produced from the manufacture of phthalocyanine dyes and pigments.

The phthalocyanine dyes and pigments are brilliant blues and greens that are stable with respect to heat and light, acid, and alkali. They are used in paints, lacquers, inks, plastics, and rubber. For fiber dyeing, the phthalocyanine pigments can be made into temporarily soluble dyes that are subsequently insolubilized on and in fibers. Soluble phthalocyanine pigment precursors can be printed on fiber and cured with heat to form the insoluble pigments. Solubilizing groups, such as sulfonates, can be added to make direct dyes for paper, cotton, and other textile fibers. Finally, additional chemical modification can add fiber-reactive groups for dyeing cotton.

Table 1 gives the 1979 production data for the 13 commercially significant phthalocyanine dyes and pigments included in this study--dyes produced at greater than 2.3 metric tons and pigments produced at greater than 0.5 metric tons. Production data are for the commercial product, which may include solvents and other diluents and impurities in addition to the specific dye chemical of interest. Concentration of the organic dye or pigment in the commercial product may vary from 10% to 100%. Table 1 is arranged according to the Colour Index (C.I.) number (Colour Index, The Society of Dyers and Colourists, 1980). The 1979 production levels were taken from the Organic Dyes and Pigments Data Base prepared by SRI International (Swett et al., 1983).

Table 1

PHTHALOCYANINE DYES AND PIGMENTS
INCLUDED IN THIS STUDY

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
74100	Pigment Blue 16	> 0.5
74160	Pigment Blue 15, 15:1, 15:2, 15:3, 15:4	6562
74180	Direct Blue 86, 199[a]	> 475
74260	Pigment Green 7	1475
74265	Pigment Green 36	161
74460	Reactive Blue 7	> 2
-	Direct Blue 189	> 2
-	Reactive Blue 3	> 2
-	Reactive Blue 21	> 2
-	Reactive Blue 25	> 2
-	Reactive Blue 38	> 2
-	Reactive Blue 71	> 2
-	Reactive Blue 174	> 2

[a]Direct Blue 199 has no C.I. number. It is reported here because the Colour Index reports that it is similar to Direct Blue 86, C.I. 74180. 1979 U.S. commercial production of Direct Blue 86 was 470 metric tons. The production of Direct Blue 199 was reported only as greater than 5 metric tons.

For nine dyes and one pigment the production is shown only as an amount greater than a minimum number. The dyes, which are almost all reactive dyes, are produced by a single manufacturer and public sources do not list actual production values in order to protect trade secrets. Production amounts for these dyes could be substantial. The U.S. Tariff Commission (USTC, 1974) reported a total 1972 production of 628 metric tons of phthalocyanine dyes and 6350 metric tons of phthalocyanine pigments. U.S. total production of dyes and pigments by chemical class were not reported for 1979 (USITC, 1980), but adding the quantities in Table 1 shows a total dye production of greater than 491 metric tons and a total pigment production of greater than 8198 metric tons. Thus, pigment production grew substantially (29% minimum) in the seven-year period. If phthalocyanine dye production grew as much, it would have been 810 metric tons, which would mean that production of phthalocyanine dyes would have increased by 182 metric tons from 1972 to 1979.

The U.S. International Trade Commission does provide data on the total U.S. sales and imports of reactive dyes as a class. If inventory changes are assumed to be minimal, then U.S. sales minus U.S. imports would be a measure of U.S. production. On this basis, reactive dye production grew by 21% in the years from 1973 to 1980. Even though not all reactive dyes are phthalocyanine dyes, this is corroborating evidence that the confidential production figures for the phthalocyanine reactive dyes could be substantial unless the share of the reactive dye market held by phthalocyanine dyes has decreased.

For seven of the dyes covered in this study, no C.I. Number is available. This means that the complete chemical composition of the dye has not been disclosed. Any discussion of the wastes produced by manufacture of these seven dyes will be incomplete because some of the dye intermediates and the chemical and physical processing steps required are unknown.

In the following sections of this report the process chemistry of the phthalocyanine dyes and pigments and sources of wastes during dye and pigment manufacture are discussed in detail.

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of phthalocyanine dye and pigment production, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye and pigment intermediates.
- Solid residues from product synthesis, solvent distillation, and filtration. These would contain unreacted dye and pigment intermediates, reaction by-products, and heavy metals such as iron and zinc. Reaction by-products could include polychlorinated biphenyls (PCBs).
- Gaseous emissions that may contain ethylene oxide, formamide, arylamines, and chlorinated aromatic solvents.
- Process wastewaters that may contain mother liquor from filtering operations. These may contain organic materials and heavy metals from the various synthesis steps and PCBs might be present.
- Wastewater treatment solids. The solids may be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves, some reaction by-products (including PCBs), and inorganic elements.

The information on the producers of the dyes and pigments was analyzed to choose a few representative producers where a sampling program might be conducted to determine the composition of the waste emissions. The following producers are recommended:

ICI Americas Inc., Chemical Specialties Co.
American Hoechst Corp., Industrial Chemicals Division
Sun Chemical Corp.
Ciba-Geigy Corp.
American Cyanamid Co. (Marietta, OH, plant)
Toms River Chemical Corp.

ICI and American Hoechst were chosen because they make the majority of the commercially significant reactive dyes. Sun, Ciba-Geigy, and American Cyanamid were chosen because they each make many of the commercially significant pigments, so that sampling all three producers could give a measure of how different manufacturing and waste management practices affected waste emissions. Toms River was included because it manufactures one of the reactive dyes and two of the commercially significant direct dyes.

SECTION 3

PROCESS CHEMISTRY

INTRODUCTION

Phthalocyanines are blue and green pigments and dyes that are based on a 16-member ring system containing both carbon and nitrogen atoms. The ring system is very similar to the porphin ring that is the basis for chlorophyll and hemin (the iron-based pigment in hemoglobin). The phthalocyanine pigments were discovered by accident in 1928 during preparation of phthalonitrile from phthalic anhydride and ammonia in an iron reaction kettle. The blue pigment iron phthalocyanine was formed as an impurity. Subsequently, it was discovered that phthalocyanine could be produced with the alkali metal and alkaline earth metal elements (including sodium and calcium), other metals (including copper, zinc, cadmium, mercury, and aluminum), and the transition elements (including iron and nickel). When the phthalocyanine pigments were commercialized, the dominant material was based on copper. Five of the six dyes and pigments with known compositions and known production values shown in Table 1 contain copper. The sixth is a copper-free pigment. Based on the discussion of dye chemistry contained in Abrahart (1977), Allen (1971), and Venkataraman (1952, 1972), it seems reasonable to assume that many of the dyes with unknown composition are also copper-based.

Phthalocyanine pigments can be made into water-soluble dyes by sulfonation. It is also possible to prepare some soluble phthalocyanine dyes from substituted phthalic anhydrides (Venkataraman, 1952). For example, Allen (1971) describes procedures in which chloromethyl groups are introduced onto the phthalocyanine molecule. These can be converted to water-soluble derivatives that can readily be converted on the fiber to water-insoluble derivatives. The chemistry of the substituted phthaolcyanines is not discussed further because there is no evidence that it is used for the dyes included in this study.

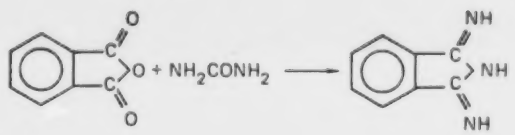
The basic phthalocyanine molecule can be prepared by several routes. Two prominent ones include the reaction between copper salts and phthalonitrile and the reaction between phthalic anhydride, urea, and copper salts in an organic solvent. This latter process is described in this section to illustrate the chemical and processing operations that are required.

Halogenation of copper phthalocyanine is described next in some detail because it is the basis for one way of producing pigments that are stable in solvents and because it converts blue phthalocyanine pigments to green pigments. Pigment processing used to produce material for water- and solvent-

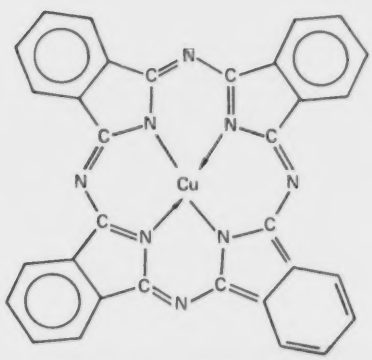
based applications is then described. Sulfonation is described because it is an important way of converting insoluble phthalocyanine pigments into water-soluble dyes. Finally, the important class of fiber reactive phthalocyanine dyes is discussed.

PREPARATION OF COPPER PHTHALOCYANINE BY THE PHTHALIC ANYDRIDE/UREA PROCESS

In this process, the phthalonitrile is generated <u>in situ</u> by the action of urea on phthalic anhydride or related materials such as phthalimide or phthalamide:



Phthalic Anhydride Urea Diiminoisoindoline



Copper Phthalocyanine

The reaction proceeds via numerous intermediates. The diiminoisoindoline shown above is highlighted because it can be isolated from the reaction mixture and used, along with copper salts and a suitable solvent,* to make a textile printing material (C.I. Ingrain Blue 2) that forms an insoluble copper

*Allen (1971) indicates that dihydric alcohols, such as ethylene glycol, and amides, such as formamide, have been used.

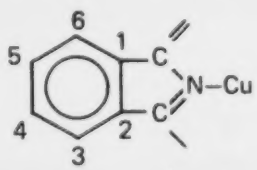
phthalocyanine pigment upon steaming. In early versions of the urea process, the phthalic anhydride (or phthalimide or phthalamide) and urea were heated together to above 140°C to form a molten reaction mass. Copper phthalocyanine formed in the presence of copper chloride (cuprous or cupric) and catalysts that included boric acid and ammonium molybdate. The copper phthalocyanine formed was a solid at the temperatures used and was difficult to remove from the reactor. A solvent-based process was developed to solve this problem. The dye intermediates, along with arsenic pentoxide or ferric and aluminum chlorides as catalysts were heated at 160°C to 200°C for 5 hours in an agitated reactor with a non-volatile solvent. The solvent does not dissolve the copper phthalocyanine formed, but does cause the pigment to form as a slurry of crystals that can be filtered out of the reaction mixture. The filter cake is dried to remove residual solvent and then purified by resuspending it in dilute hydrochloric acid and refiltering, followed by washing and drying (Venkataraman, 1952). C.I. Pigment Blue 15 (C.I. 74160) is probably prepared in this way.

Trichlorobenzene has been the solvent most often used, but nitrobenzene and polyalkyl benzene (Uyeta et al., 1976) as well as kerosene (Versar, 1978) can also be used. The trichlorobenzene has been identified as the source of polychlorinated biphenyl (PCB) in phthalocyanine pigments (EPA, 1979; Uyeta et al., 1976; DCMA, 1981; Anliker, 1981.) The reactions involved are not completely understood but seem to involve a condensation of two trichlorobenzene molecules that is catalyzed by the copper. High PCB levels have been reported. One United States study of phthalocyanine pigments (Anliker, 1981) reported an average contamination level of 100 ppm with a large number of values between 100 and 500 ppm. A study of Japanese phthalocyanine pigments (Uyeta et al., 1976) yielded similar results.

The PCB concentrations can be decreased by switching solvents or by instituting other process changes (EPA, 1979; DMCA, 1981; Versar, 1978). An effective process change would be to reintroduce the solvent-free process. It has been reported that these modifications can reduce levels below 50 ppm (Versar, 1978).

PREPARATION OF HALOGENATED PHTHALOCYANINES

Copper phthalocyanine can be readily halogenated. Adding halogens changes the color and affects the crystalline form of the pigment. The carbon atoms in the aromatic ring associated with one quarter of a copper phthalocyanine molecule are shown below to illustrate the numbering convention used with phthalocyanine compounds:



In the other three benzene rings the numbers are $1'$, $2'$; $1''$, $2''$, and so forth. The magnitude of the color change depends on the extent and position of halogenation. Chlorination takes place first at the 4 and 5 positions with little change in color. Thus 4,4',4'',4''',5,5',5'',5'''-octachloro copper phthalocyanine would still be blue (Venkataraman, 1952). Lightly chlorinated (8 or fewer chlorines) copper phthalocyanine can be prepared in a blue α crystalline form, which is a good pigment and will not revert in solvents to the β crystalline form, which is often a poor pigment. (Crystal forms are discussed more completely below under PIGMENT PROCESSING.)

Chlorine in the 3 and/or 6 position causes a color shift to green. The 3 and 6 positions are harder to chlorinate than the 4 and 5 positions; thus the color of the chlorinated copper phthalocyanine pigment can be controlled by the time and severity of chlorination.

The following method was most often mentioned for obtaining chlorinated copper phthalocyanine. The purified pigment is suspended in a eutectic mixture of aluminum chloride and sodium chloride in an autoclave that is heated to 180°-200°C. Chlorine is introduced as a gas. Twenty hours are required (Venkataraman, 1952) to add 15 to 16 chlorine atoms per pigment molecule. When polychlorinated biphenyls contaminants are present, they also will be chlorinated and can become decachlorobiphenyl (Uyeta, et al., 1976). The hot reaction mass is quenched in cold water, Acidified, and the insoluble pigment is separated from the soluble aluminum and sodium salts by filtration. The pigment C.I. Pigment Green 7, C.I. 74260, is probably produced by this route. The timing to produce pigment with eight or fewer chlorines per molecule has not been disclosed.

Mixed halogen pigments containing both bromine and chlorine atoms can be produced by using bromine gas instead of chlorine in the aluminum chloride/sodium chloride melt. C.I. Pigment Green 36, C.I. 74265, which is a hexabromodecachloro copper phthalocyanine, is probably produced this way.

PIGMENT PROCESSING

The unchlorinated material prepared by the phthalonitrile or phthalic anhydride/urea process is not suitable for use as a pigment without further treatment because the pigment crystallizes into what is known as the β form, which consists naturally of long needles that do not have good covering properties. Basically, two physical processes are used to prepare useful pigment material in the α form which has good covering properties: the sulfuric acid process and grinding process. In the sulfuric acid process the purified β form pigment is dissolved in concentrated sulfuric acid and then transferred rapidly into another tank containing water (drowned). The pigment recrystallizes into very small crystals of the α form. In the grinding process (Allen, 1971), the β form pigment is ground with crystalline material, such as sodium chloride, and an organic solvent, such as acetone or trichlorobenzene, to convert the pigment to the α form. The solvent and salt can be removed by resuspending the ground pigment in water, filtering, and washing (Allen, 1971). The α form, however, cannot be used in aromatic

solvent systems, whereas the β form can. As was discussed previously, however, partial chlorination of the pigment can be used to stabilize the α form in solvent systems.

It is also possible to prepare a β form pigment with good covering properties for aromatic solvent systems (Allen 1971) by

- Grinding either the α or β form with salt in the presence of crystallizing solvents.* This grinding must be carefully controlled to avoid producing the α form pigment which would not be stable in an aromatic solvent system.
- Treating ground α form with a crystallizng solvent. Careful control is required achieve conversion to a β form with short needles and good pigment properties.

The α form would normally be considered the more cost-effective pigment because it can be prepared more easily than a suitable β form. The β form is greener, however, and might be preferred in some applications regardless of cost.

The availability of C.I. Pigment Blue 15 (C.I. 74160) in several variations is evident that several different processing schemes may be used to prepare the same basic pigment for market. In addition to the material sold as C.I. Pigment Blue 15, which is the α form prepared by the sulfuric acid process, four other forms are sold: (Moser, 1973)

C.I. Pigment Blue 15:1	Partially chlorinated (α form stabilized) and suitable for solvent-based uses.
C.I. Pigment Blue 15:2	Partially chlorinated (α form stabilized) and specially treated to prevent flocculation in solvent based paints.†
C.I. Pigment Blue 15:3	Pigment grade β form, which is naturally stable in solvent-based uses.
C.I. Pigment Blue 15:4	Pigment grade β form chemically treated to prevent flocculation in solvent based paints.

PREPARATION OF SULFONATED PHTHALOCYANINES

Direct dyes are produced by adding solubilizing groups onto the phthalocyanine molecule. The most direct method, sulfonation, is used to

---

*Lubs (1955) reports that acetone, tetrachloroethylene, and o-dichlorobenzene are suitable.

†Lubs (1955) indicates that aluminum benzoate may be used to prevent flocculation.

produce C.I. Direct Blue 86 (C.I. 74180) and C.I. Direct Blue 199. Partial sulfonation is achieved by reacting a purified phthalocyanine pigment with 26% oleum for 12 hours at 60°C, which adds 2 sulfonic acid groups. The product is neutralized and salted out. More complete sulfonation can be achieved by using chlorosulfonic acid at 130°C for 5 to 6 hours to add four sulfochloride groups to the molecule. All four groups go onto the 3 position of each aromatic ring. The reaction mixture is cooled to 0°C with ice water, and then the dye is precipitated by adding sodium chloride. The dye is filtered and washed with a cold sodium chloride solution. The paste that results contains dye molecules with a mixture of sulfochloride and sulfonic groups because the sulfochloride group is hydrolyzed by water. Venkataraman (1972) reports that both trisulfochloride-monosulfonic acid and disulfochloride-disulfonic acid are present in the paste. Of course, more complete hydrolysis can be achieved by allowing longer contact with water. Amides can be prepared by reacting the sulfochloride with ammonia or amines (Roberts and Caserio, 1965).

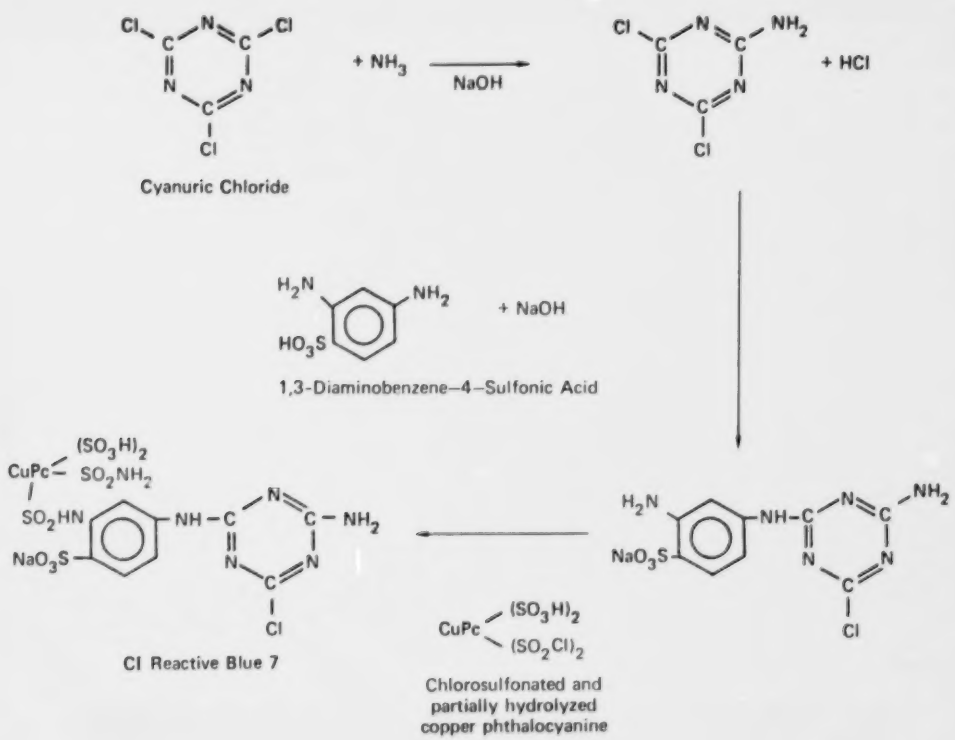
REACTIVE DYES

Two major types of reactive dye are prepared from phthalocyanine. One type was developed originally by ICI as the Procion dyes and further developed by CIBA as the Cibacron dyes. These dyes are based on attaching a dichloro or monochloro triazinyl group to a sulfonated phthalocyanine molecule. The sulfonates provide solubility and the chlorines on the triazinyl group react with hydroxyl groups on fibers to give an ether linkage between the dye and the fiber. In the other type, developed by Farbwerke Hoechst and sold as Remazol dyes, a β-sulphatoethyl sulfone group is attached. Under alkaline conditions, the sulfatoethyl group decomposes into a vinyl group that then forms an ether linkage with hydroxyl on the fiber.

Synthesis of Procion or Cibacron Reactive Dyes

These dyes use a variety of diamino derivatives of aromatic compounds to link the reactive monochloro or dichloro triazinyl group to copper phthalocyanine. The one dye of this class with a known structure is C.I. Reactive Blue 7 (Cibacron Turquoise Blue G). No specific recipe for preparing this dye was found, but a general procedure described by Venkataraman (1972) is probably used. As is illustrated below, cyanuric chloride (2,4,6-trichloro-s-triazine) is first reacted with ammonia in aqueous solution to yield 2-amino-4,6-dichloro-s-triazine. This is then reacted with 1,3-diaminobenzene-4-sulfonic acid to yield a product with the monochloro triazinyl group attached to a benzene sulfonic acid group that has one reactive amine group left. A paste of copper phthalocyanine (symbolized by CuPc) that has been reacted with chlorosulfonic acid and then partially hydrolyzed to a mixed sulfonic acid-sulfochloride form is added. The sulfochloride group reacts with the remaining amine group on the benzene sulfonic acid to form the reactive dye product. Ammonia is added to convert any remaining sulfochloride to the sulfamide. The completed dye is precipitated by adding sodium chloride, then filtered, and dried. The other three Procion dyes shown in Table 1 (C.I. Reactive Blue 3, Procion Turquoise

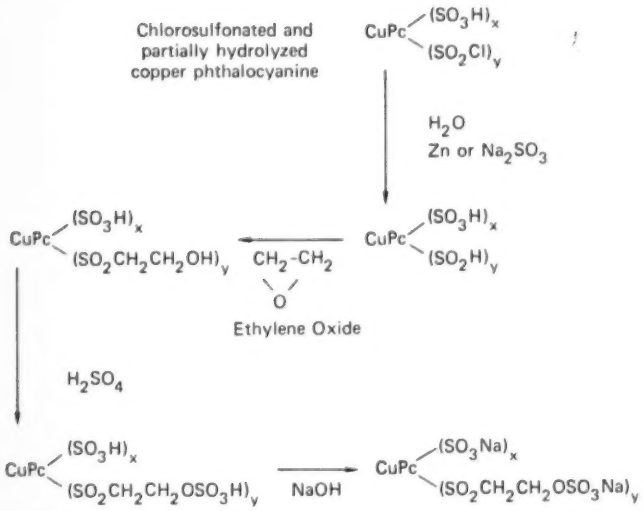
w-7G; C.I. Reactive Blue 174, Procion T Turquoise T-2G; and C.I. Reactive Blue 71, Procion Turquoise H-A) are probably made in a similar manner, either with a different link between the dye and the reactive group or using a different source for the reactive group (such as 2,4,6-trichloropyrimidine) in place of the cyanuric chloride.



Synthesis of Remazol Reactive Dyes

The chemical composition of the two Remazol dyes shown in Table 1 (C.I. Reactive Blue 21, Remazol Turquoise Blue B; and C.I. Reactive Blue 38, Remazol Brilliant Green 6B) is unknown. Venkataraman (1972) reports that in some the sulfatoethyl sulfone group is attached directly to the metal phthalocyanine, whereas in others there may be intervening groups such as an aryl amine. The steps required to put a sulfatoethyl sulfone group directly on the phthalocyanine are shown below to illustrate the chemistry involved. A paste of chlorosulfonated copper phthalocyanine, which will contain some sulfonic acid groups that result from hydrolysis of the sulfochloride groups, is mixed in a reactor with water and zinc or sodium sulfite. The chlorosulfonic groups are reduced to sulfinic acid. Ethylene oxide is bubbled through the solution. It reacts with the sulfinic acid to form a

β-hydroxyethyl sulfone. The hydroxyl group is then esterified to form a mono ester with sulfuric acid and then converted to the sodium salt with sodium hydroxide. The completed reactive dye is precipitated by adding sodium chloride, then filtered and dried.



SECTION 4

ORGANIC AND INORGANIC INTERMEDIATES, REAGENTS, AND CATALYSTS USED IN PHTHALOCYANINE DYE AND PIGMENT PRODUCTION

Information on the intermediates, reagents, and catalysts required to produce the phthalocyanine dyes and pigments listed in Table 1 was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980), Allen (1971), Lubs (1955), and Venkataraman (1952, 1972). The organic intermediates and solvents and inorganic intermediates and catalysts are listed in Table 2. Table 2 also identifies those substances which, if present in solid wastes, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). These substances are identified by their hazard code.

All possible intermediates are listed for the dyes of known process chemistry, even though some intermediates may be required for syntheses that are not widely used commercially. All the chemicals that were identified as being used in pigment processing are included, although it is recognized that all might not be used by a single manufacturer and that the list is not exhaustive because proprietary chemicals may not be included. In some cases, chemicals are shown that dye chemistry texts indicate might be required for synthesis of reactive dyes. There is no direct evidence that these particular chemicals are used to produce the six commercially significant reactive dyes with unknown composition that are shown in Table 1, but their use is considered highly probable.

Table 2

ORGANIC AND INORGANIC CHEMICALS REQUIRED FOR THE MANUFACTURE OF PHTHALOCYANINE DYES AND PIGMENTS

Organic Intermediates and Solvents	Hazardous Waste Listing[a]
Acetone	I, T
Benzoic acid, aluminum salt	
Cyanuric chloride	
1,3-Diaminobenzene-4-sulfonic acid	
Dichlorobenzene	T
Ethylene oxide[b]	I, T
Methanol	T
Phenol[c]	T
Phthalamide[c]	
Phthalic anhydride	T
Phthalimide[c]	
Phthalonitrile	
Trichlorobenzene	
Urea	

[a] Hazard codes from the Federal Register (1980) indicate the basis for EPA listing the material hazardous: Ignitable (I) and Toxic (T).

[b] Probable requirements for reactive dyes for which no specific chemical composition or process information was available.

[c] Not required for synthesis routes assumed, but can be used in alternative routes.

Table 2 (Concluded)

Inorganic Materials	Hazardous Waste Listing[a]
Aluminum chloride	
Ammonia	
Ammonium molybdate	
Arsenic oxide	
Bromine	
Chlorine	
Chlorosulfonic acid[b]	
Cupric chloride	
Cuprous chloride[c]	
Ferric chloride	
Sodium carbonate	
Sodium chloride	
Sodium hydroxide	
Sulfuric acid	

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, though, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture are present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residues, and the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent and some is discharged on wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 1 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce phthalocyanine dyes and pigments consists of stationary reaction kettles (steel or glass-lined, with heavy-duty agitators), and standard filter presses, vacuum filters, grinders, dryers, and blenders (Steadman et al., 1977).

The basic reaction sequence for a phthalocyanine pigment can be quite involved, including reaction of the intermediates in an organic solvent to form the metal (typically copper) phthalocyanine, purification of the pigment by filtering and drying (to remove the trichlorobenzene and volatile unreacted intermediates), and then washing and filtering to achieve higher purity. If halogenation is used, the product is separated from the aluminum chloride/sodium chloride melt by quenching in water, followed by filtration. Preparation of α form pigment will often require dissolution of purified pigment in concentrated sulfuric acid, followed by drowning in water, filtration, and washing.

Preparation of phthalocyanine dyes often requires sulfonation of a purified pigment followed by filtering and washing, which may be followed by one or two sets of reacting, filtering, and washing in series when reactive dyes are produced.

The sources of wastes from dye manufacture identified in Figure 1 are summarized below:

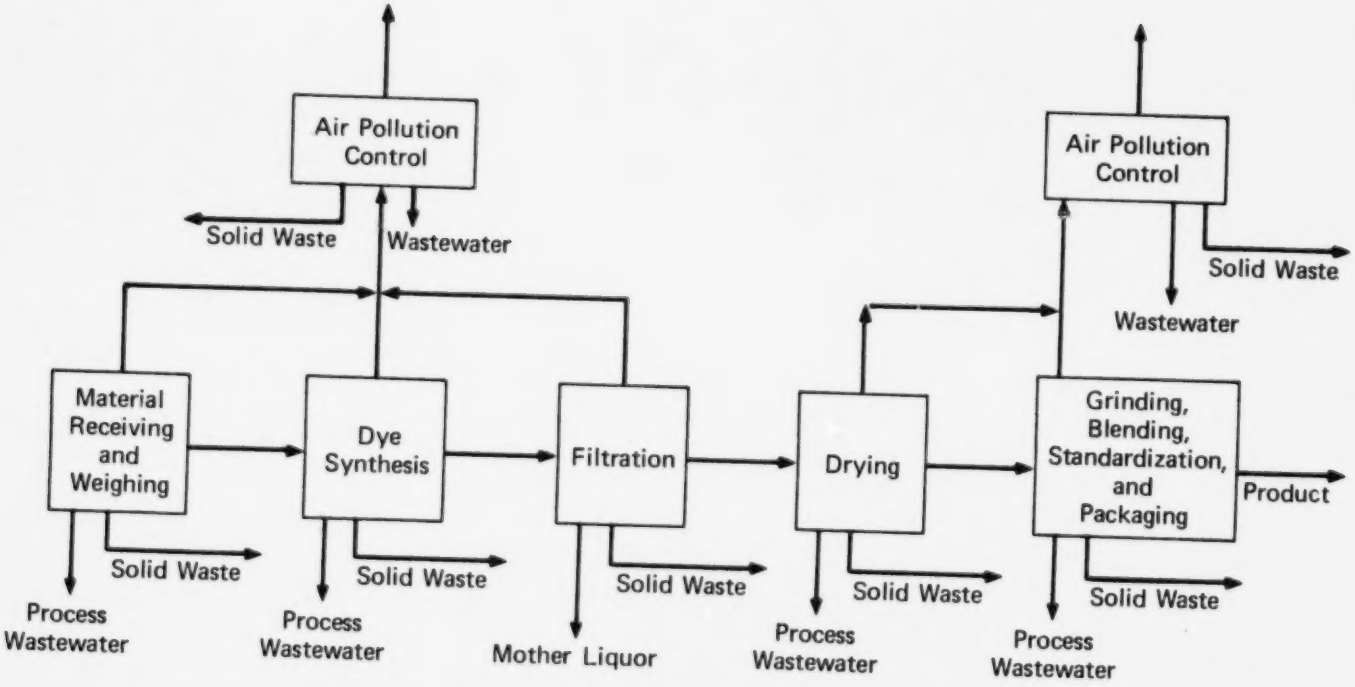


FIGURE 1 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

- Material handling--Air emissions from raw material dusting and volatilization, solid residues on shipping containers, and process wastewaters from equipment washdown.
- Dye syntheses--Air emissions from the volatilization of intermediates, by-products, and solvent from reaction vessels, solid residues from solvent recovery stills, and process wastewaters from equipment washdown.
- Product and intermediate filtration--Air emissions from unreacted intermediate, by-product, and solvent volatilization during material handling, solid residues from spills, and process wastewater from equipment washdown. A significant additional source of process wastewater is the mother liquors from the multiple filtrations required to produce purified product.
- Drying--Air emissions from volatilization of by-products and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye. Trichlorobenzene may be a significant potential air emission because it is used in the metal phthalocyanine synthesis.
- Grinding, blending, standardization, and packaging--Solid residues from dusts produced by the grinding operations that may be either in the air streams from vent systems designed to prevent the material from entering the workplace environment or in the solid residue from spills. For phthalocyanine pigments, grinding is not always the final step before blending. Production of useable β form pigments or α form pigments can involve grinding with both salt and an organic solvent. These are washed from the ground pigment, creating a brine that may contain more than a few parts per million of organic solvent. The treated pigment is then dried and blended, standardized, and packaged. Some phthalocyanine pigment is flushed into oils such as boiled linseed oil (Lubs, 1955). Since flushing involves contacting a wet press cake with oil and boiling out the water while the two are mixed together, an organic-contaminated condensate is produced.
- Air pollution control--Solid residues from baghouses or scrubbers collecting fine dusts and process wastewater from scrubbers.

MATERIAL IN THE WASTE STREAMS FROM PHTHALOCYANINE DYE AND PIGMENT PRODUCTION

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, primarily because it contains the mother liquors from the various aqueous processing steps.

On the basis of the chemistry discussed in Section 3, these mother liquors will probably contain unreacted intermediates, reaction by-products (such as the polychlorinated biphenyls that may be formed when some chlorinated solvents are used), unprecipitated dye or pigment, and salts. The salts may include the sodium chloride, expected from salting out and grinding; aluminum chloride from halogenation; excess copper chloride; sodium and

ammonium sulfates from neutralization reactions; and iron, arsenic, and molybdenum salts from spent catalysts. Additional organics may be present from solvents used in processing, such as trichlorobenzene, dichlorobenzene, and acetone. Wastewater treatment may cause some of the less soluble components to adsorb on wastewater treatment solids.

When reactive dyes are manufactured, the opportunities for finding a variety of organics in the wastewater increase. Reactive dyes use highly reactive intermediates, such as cyanuric chloride, trichloropyrimidine and ethylene oxide. If primary reactions are not complete or if excess ingredients are used, these reactive intermediates can react with the other intermediates and water. For example, ethylene oxide can react with water to form ethylene glycol and with ammonia and organic amines to form ethanolamines (Roberts and Caserio, 1965).

Table 3 lists the phthalocyanine dyes and pigments produced in 1979 for which chemical compositions were available. The wastes estimated to be produced by the manufacture of these materials are also shown in the table. In some cases there are several process alternatives and only a probable route could be identified. For the production of the basic copper phthalocyanine, a solvent-based phthalic anhydride/urea process utilizing trichlorobenzene was assumed. For the production of metal-free phthalocyanine, a methanol extraction of sodium phthalocyanine was assumed.

Table 3 does not include an exhaustive list of the reaction by-products that are likely to be present. By-products were not within the scope of this study because, except for the polychlorinated biphenyls, little useful information regarding the amount or nature of these by-products was found. The producers of the dyes and pigments are indicated by letter code in the Table 3. Table 4 gives the full names of the producers associated with the letter codes in Table 3. Table 5 lists the producers of phthalocyanine dyes and pigments and the phthalocyanine products they manufacture. The identity and corporate ownership of the producers is based on 1979 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 4 and 5. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete.

Table 3

ORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF PHTHALOCYANINE DYES AND PIGMENTS OF KNOWN MANUFACTURING PROCESS

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
CGY	74100	Pigment Blue 16	> 0.4	Pigment Blue 16 Methanol Phthalic anhydride Trichlorobenzene Urea Unknown by-products
ACY, AMS, APO BAS, BOR, BUC CGY, CIK, DUP HRC, HRS, HSH HST, ICC, IDC MGR, POP, ROM SDH, SNA, TMS USM	74160	Pigment Blue 15, 15:1, 15:2, 15:3, 15:4	6562	Pigment Blue 15 Pigment Blue 15 (chlorinated) Acetone Aluminum benzoate Dichlorobenzene Phthalic anhydride Trichlorobenzene Urea Unknown by-products
AC, ATL, BAS BDO, CK, DUP FAB, TRC, VPC	74180	Direct Blue 86 Direct Blue 199	> 475	Direct Blue 86 Direct Blue 199 Phthalic anhydride Trichlorobenzene Urea Unknown by-products

Table 3 (Concluded)

1979 U.S. Commercial Producers	C. I. No.	C. I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
ACY, ALG, BAS CGY, CIK, DUP HST, POP, SDH SNA, TMS	74260	Pigment Green 7	1475	Pigment Green 7 Phthalic anhydride Trichlorobenzene Urea Unknown by-products
ACY, CGY, DUP HRC, HST, SNA	74265	Pigment Green 36	161	Pigment Green 36 Phthalic anhydride Trichlorobenzene Urea Unknown by-products
TRC	74460	Reactive Blue 7	> 2	Reactive Blue 7 Cyanuric chloride 1,3-Diaminobenzene-4-sulfonic acid Phthalic anhydride Trichlorobenzene Urea Unknown by-products

Table 4

DIRECTORY OF DYE AND ORGANIC PIGMENT MANUFACTURERS, 1979

Names of manufacturers that reported production and/or sales of phthalocynamine dyes and pigments to the U.S. International Trade Commission for 1979 are listed below in order of their identification codes as used in Table 3.

Code	Name of Company
Dye Manufacturers	
AC	American Color & Chemical Corp.
ATL	Atlantic Chemical Corp.
BAS	BASF Wyandotte Corp., Pigments Div.
BDO	Benzenoid Organics, Inc.
CK	Crompton & Knowles Corp., Dyes & Chemical Div.
DUP[a]	E.I. duPont de Nemours & Co., Inc.
FAB	Fabricolor Manufacturing Corp.
HST	American Hoechst Corp., Industrial Chemicals Div.
ICI	ICI Americas, Inc., Chemical Specialties Co.
TRC[b]	Toms River Chemical Corp.
VPC	Mobay Chemical Corp., Dyestuff Div.
Pigment Manufacturers	
ACY	American Cyanamid Co.
ALG	Allegheny Chemical Corp.
AMS	Ridgway Color & Chemical
APO	Apollo Colors, Inc.
BAS	BASF Wyandotte Corp., Pigments Div.
BOR	Borden, Inc., Printing Ink Div., Pigments Div.
BUC	Synalloy Corp., Blackman Uhler Chemical Div.
CGY	Ciba-Geigy Corp.
CIK	Flint Ink Corp., Cal/Ink Div.

Table 4 (Concluded)

Pigment Manufacturers	Name of Company
DUP	E.I. duPont de Nemours & Co., Inc.
HRC	Harmon Colors Corp.
HSH	Harshaw Chemical Co.
HST	American Hoechst Corp., Industrial Chemicals Div.
ICC	Inmont Corp.
IDC	Industrial Color, Inc.
MGR	Magruder Color Co., Inc.
POP	Pope Chemical Corp.
ROM	United Merchants & Manufacturers, Inc., Roma Chemical Div.
SDH	Sterling Drug, Inc., Hilton-Davis Chemical Co. Div.
SNA	Sun Chemical Corp.
TMS	Sterling Drug, Inc., Thomasset Colors Div.
USM	USM Corp., Bostik Div., Southern Region

[a] In 1979, DuPont sold its paper dye operations to Mobay Chemical Corp. and its textile dye operations to Ciba-Geigy Corp. and Crompton Knowles Corp.

[b] In 1979, 80% of Toms River Chemical Corp. was owned by Ciba-Geigy and 20% was owned by Sandoz AG. In mid-1981, Sandoz sold its interest to Ciba-Geigy.

Table 5

1979 PRODUCERS OF PHTHALOCYANINE DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
74180	Direct Blue 86
American Cyanamid Co.	
74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74160	Pigment Blue 15:4
74260	Pigment Green 7
74265	Pigment Green 36
Allegheny Chemical Corp.	
74260	Pigment Green 7
Atlantic Chemical Corp.	
74180	Direct Blue 86
Ridgway Color & Chemical	
74160	Pigment Blue 15:3
Apollo Colors, Inc.	
74160	Pigment Blue 15:3
BASF Wyandotte Corp., Pigments Div.	
74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74160	Pigment Blue 15:4
BASF Wyandotte (continued)	
74260	Pigment Green 7
-	Direct Blue 199
Benzenoid Organics, Inc.	
74180	Direct Blue 86
Borden, Inc., Printing Ink Div., Pigments Div.	
74160	Pigment Blue 15:3
Synalloy Corp., Blackman Uhler Chemical Div.	
74160	Pigment Blue 15:3
Ciba-Geigy Corp.	
74100	Pigment Blue 16
74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74160	Pigment Blue 15:4
74260	Pigment Green 7
74265	Pigment Green 36
Flint Ink Corp., Cal/Ink Div.	
74160	Pigment Blue 15:3
74260	Pigment Green 7
Crompton & Knowles Corp., Dyes & Chemical Div.	
74180	Direct Blue 86

Table 5 (Continued)

E.I. duPont de Nemours & Co., Inc.[a]

74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74160	Pigment Blue 15:4
74180	Direct Blue 86[a]
74260	Pigment Green 7
74265	Pigment Green 36
-	Direct Blue 199[a]

Fabricolor Manufacturing Corp.

74180	Direct Blue 86

Harmon Colors Corp.

74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74265	Pigment Green 36

Harshaw Chemical Co.

74160	Pigment Blue 15

American Hoechst Corp., Industrial Chemicals Div.

74160	Pigment Blue 15
74160	Pigment Blue 15:1
74260	Pigment Green 7
74265	Pigment Green 36
-	Reactive Blue 21
-	Reactive Blue 38

Inmont Corp.

74160	Pigment Blue 15:3

ICI Americas, Inc., Chemical Specialties Co.

-	Reactive Blue 3
-	Reactive Blue 25
-	Reactive Blue 71
-	Reactive Blue 174

Industrial Color, Inc.

74160	Pigment Blue 15:3

Magruder Color Co., Inc.

74160	Pigment Blue 15:3

Pope Chemical Corp.

74160	Pigment Blue 15:3
74260	Pigment Green 7

United Merchants & Manufacturers, Inc., Roma Chemical Div.

74160	Pigment Blue 15:3

Sterling Drug, Inc., Hilton-Davis Chemical Co. Div.

74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74260	Pigment Green 7

Sun Chemical Corp.

74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74160	Pigment Blue 15:3
74160	Pigment Blue 15:4
74260	Pigment Green 7
74265	Pigment Green 36

Table 5 (Concluded)

Sterling Drug, Inc., Thomasset Colors Div.	
74160	Pigment Blue 15
74160	Pigment Blue 15:1
74160	Pigment Blue 15:2
74260	Pigment Green 7
Toms River Chemical Corp.[b]	
74180	Direct Blue 86
74460	Reactive Blue 7
-	Direct Blue 189
USM Corp., Bostik Div., Southern Region	
74160	Pigment Blue 15
Mobay Chemical Corp., Dyestuff Div.	
74180	Direct Blue 86

[a] In 1979 DuPont sold its paper dye operations to Mobay Chemical Corp. and its textile dye operations to Ciba-Geigy Corp. and Crompton & Knowles Corp.

[b] In 1979, 80% of Toms River Chemical Corp. was owned by Ciba-Geigy and 20% was owned by Sandoz AG. In mid-1981 Sandoz sold its interest to Ciba-Geigy.

REFERENCES

Allen, R.L.M. 1971. Colour Chemistry. Appleton Century Crofts Educational Division, Meredith Corporation, New York.

Abrahart, E. M. 1977. Dyes and Their Intermediates. Chemical Publishing Co., Inc., New York.

Anliker, R. 1981. Concerning the Polychloro Biphenyls (PCBs) in Synthetic Organic Pigments. Swiss Chem, 3: 25-29.

BIOS (British Intelligence Objectives Subcommittee). 1945. German Dyestuffs and Dyestuffs Intermediates; Anthrasols, Heliogens, Sirius Light Blue Dyestuffs. Final Report No. 960, H. M. Stationery Office, London.

Bomberger, D. C., and R. L. Boughton. 1983. Wastes from Manufacture of Dyes and Pigments (Benzidine and Its Congeners Subsector). U. S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. Contract No. 68-03-2934.

DCMA (Dry Color Manufacturers Association). 1981. Polychlorinated Biphenyls Unintentionally Generated in the Manufacture of Diarylide and Phthalocyanine Pigments. Testimony submitted to the U.S. Environmental Protection Agency in response to ANPR (Federal Register 46, 27617, May 20, 1981) to exclude PCB's below 50 ppm in manufacturing prohibitions of TSCA.

EPA. 1979. Support Document/Voluntary Environmental Impact Statement and PCB Manufacturing, Processing, Distribution in Commerce, and Use Ban Regulation: Economic Impact Analysis. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Federal Register. 1979. Polychorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions, 44(108): 31535 (May 31, 1979).

Federal Register. 1980. Identification and Listing of Hazardous Waste, 45(98): 33133.

Lapp, J. W., T. L. Ferguson, G. Gadberry, F. Hoffmeister, T. Hopkins, and B. Thompson. 1979. A Preliminary Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives. Midwest Research Institute.

Lubs, H. S. 1955. The Chemistry of Synthetic Dyes and Pigments. Reinhold Publishing Corporation, New York.

Moser, Frank H. 1973. "Phthalocyanine Blue Pigments" in Pigment Handbook. Vol. 1, Patton, T. C., ed. John Wiley and Sons, New York.

Roberts, J. D., and M. C. Caserio. 1965. Basic Principles of Organic Chemistry. W. A. Benjamin, Inc., New York.

Steadman, T. R., E. W. Helper, T. Parsons, G. E. Wilkins, and N. R. Phillips. 1977. Industrial Process Profiles for Environmental Use. Chapter 7, Organic Dye and Pigments Industry. EPA 600/2-77-023g, U.S. Environmental Protection Agency, Industrial Engineering Research Laboratory, Cincinnati, Ohio.

Swett, L., A. Twhigg, and K. E. McCaleb. 1983. The Organic Dyes and Pigments Data Base. U. S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. EPA Contract No. 68-03-2944.

The Society of Dyers and Colourists, Colour Index. Lund Humphries Printers, London, England, Volumes 1-3, Third Edition, 1971; Volume 6, Revised Third Edition, 1975, Additions and Amendments Numbers 13-36, October 1974-July, 1980.

U.S. Tariff Comission (USTC). 1974. Synthetic Organic Chemicals, U.S. Production and Sales, 1972. TC Publication 681, U.S. Government Printing Office, Washington, D.C.

U.S. International Trade Commission (USITC). 1980. Synthetic Organic Chemicals, U.S. Production and Sales, 1979. TC Publication 1099, U.S. Government Printing Office, Washington, D.C.

Uyeta, M., S. Taue, and K. Chikazawa. 1976. Polychlorinated Biphenyls in Phthalocyanine Pigments. Bulletin of Environmental Contamination and Toxicology, 16(4):417-421.

Venkataraman, K. 1952. The Chemistry of Synthetic Dyes, Volume II. Academic Press, New York.

Venkataraman, K. 1972. The Chemistry of Synthetic Dyes, Volume VI. Reactive Dyes. Academic Press, New York.

Versar, Inc. 1978. Microeconomic Impacts of the Proposed "PCB Ban Regulations." EPA 560 16-77-035, U.S. Environmental Protection Agency, Office of Planning and Management, Washington, D.C.